

Influence of Selected Physicochemical Factors on the Degradation of PAHs in Water

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Received: November 19, 2001

Accepted: January 4, 2002

Abstract

The influence of selected physicochemical factors on the degradation of five PAHs in river water and distilled water was tested.

Even in darkness, in distilled water some losses of PAHs were observed, different for various compounds, from 22% to 41% after 21 days. Aeration with air increased the losses of PAHs. But very high degradation was found when samples were irradiated with light, for some PAHs up to 90%. The loss of PAHs in river water occurred much faster than in distilled water.

The changes in PAH concentrations in distilled water could be described by first order reaction. The equation was proposed and the half-lives were calculated. In river water two stages of degradation were noticed. The different PAHs showed the different degradation, the fastest process was for benzo[a]pyrene and indeno[1,2,3-c,d]pyrene.

Keywords: PAHs, water, degradation, half-life

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants found in air, soil and aquatic environments [1, 2]. PAHs emitted into the air as a result of industrial processes enter surface waters together with atmospheric deposition. They may also be transported directly with municipal and industrial effluents [3]. Their concentrations range from more than ten ng/L in slightly contaminated water to over one thousand ng/L in heavily contaminated water [4, 5]. Some PAHs are mutagenic and potent carcinogens and their presence in surface waters can pose a risk to both human health and aquatic organisms. An important aspect of the environmental fate of PAHs is the extent to which they are accumulated in aquatic organisms [6]. PAHs are subject to degradation or dissipation through a variety of processes in aquatic environments. The changes in the concentration of PAHs in these environments are a reflection of the action of evaporation, biological degradation,

photochemical oxidation and adsorption to suspended solids with subsequent sedimentation. Sedimentation and photochemical oxidation cause a decrease in concentrations of the higher molecular weight aromatics. The lower molecular weight compounds are extensively degraded by microorganisms - bacteria, fungi and algae [7]. Mackay et al. [8] studying the stability of certain PAHs, such as fluoranthene, pyrene, benzo[a]anthracene and chrysene (4-ring hydrocarbons), such as benzo[a]pyrene, benzo[k]fluoranthene and dibenzo[a,h]anthracene (5-ring hydrocarbons) determined their half-lives in aquatic environments in the range of 1000 - 3000 h. Most studies on the degradation of PAHs have focused primarily on single compounds in distilled water [9, 10, 11].

This work studied the degradation of five PAHs in mixture: fluoranthene (Fit), benzo[a]pyrene (B[a]P), benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[k]F), and indeno[1,2,3-c,d]pyrene (I[1,2,3-c,d]P) using distilled water and natural river water. The effect of irradiation, bubbling of air, and bubbling of nitrogen in various combinations were tested on the behaviour of PAHs. The investigations were conducted in the laboratory.

Procedure

The samples were prepared from distilled water additionally purified in a Millipore purification unit. A mixture of PAH standards Mix 3 (dr Ehrenstorfer - acetonitrile solution) was added to the water so that the concentrations of individual hydrocarbons were as follows: B[a]P, B[b]F, B[k]F - 2 µg/L, whereas Fit - 5 µg/L, and I[c,d]P - 4 µg/L. Conical flasks with ground-in stoppers were washed carefully, sterilised in a dryer at 250°C and then filled with the samples.

The river water samples were prepared in the same way, but the river water was passed through a nylon membrane filter (Whatman) with a pore width of 0.45 µm to remove solid particles before adding the PAH mixture.

A tungsten lamp was used to irradiate the samples (8 h per day). Light intensity was measured with an LX-204 luxmeter (Slandi). The measurement of oxygen content was carried out in a special series of samples using Oxi 325 (WTW) dissolved oxygen meter. The nitrogen or air was passed with the flow rate of 240 mL/min for 30 min.

The concentration of the hydrocarbons added was determined in water samples immediately after their preparation (Co) and then after 3, 7, 14 and 21 days since the start of the experiment (Q). PAHs were extracted from the water samples with n-hexane. The flasks were washed twice with n-hexane because of the potential adsorption of PAHs on the vessel's walls. The extracts obtained after evaporation were dissolved in acetonitrile and analysed by HPLC with fluorescence detection. Separation and analysis were carried out on a Vydac PAH 250 x 4.6 mm column using the HP 1050 unit (Hewlett-Packard).

The investigations were performed under the following conditions: in distilled water:

- in the dark,
- in the dark with daily air saturation,
- light irradiation at the average intensity of 3500 lx,
- irradiation and daily air saturation,
- in the dark with daily bubbling of nitrogen,

and in river water:

- in the dark,
- light irradiation at an average intensity of 3500 lx,
- light irradiation and daily air saturation.

At the beginning of the experiments with daily bubbling of gases, all water samples were saturated with air or nitrogen, respectively. The study was carried out at 22 ± 1°C.

Results and Discussion

The PAHs removal from water solutions varied depending on the conditions, i.e. the type of compound, the composition of the water solution and the conditions of their exposure. The loss of the PAHs was observed in every condition (Table 1).

In the distilled water and in the dark there was a slight loss of PAHs after three days. After 21 days the concentration of Fit decreased by 22%, B[b]F and B[k]F by 28%

and I[c,d]P reaches nearly on the same level. The loss of B[a]P was the highest (41%). A higher degree of degradation of all hydrocarbons was observed in the samples which were kept in the dark but air-saturated. After 7 days the decrease of B[b]F, B[k]F, B[a]P and I[c,d]P concentrations was comparable with the one observed for those compounds after 21 days in the dark without aeration. The loss of Fit under those conditions did not exceed 25%, even after 21 days. Light irradiation caused a decrease in concentration of the tested PAHs and after 21 days the observed decrease was slightly above 90% for B[a]P and I[c,d]P, 58% and 63% for B[b]F and B[k]F, respectively, and 34% for Fit. Air saturation of the irradiated samples did not significantly affect a decrease in the concentrations of PAHs.

In river water the loss of the tested compounds proceeded considerably faster than in distilled water. This phenomenon was particularly visible within the first few days. After 21 days in the dark the concentrations of all the PAHs decreased over 50%. Irradiation significantly increased PAHs losses to above 90%, only less for Fit - 75%.

The concentration changes of PAHs in distilled water could be well described by first order kinetics with respect to the substrate. Earlier, Zepp and Schlotzhauer [13] found that the photolytic reactions of PAHs could be described by first-order rate equation. Examples of curves for PAHs losses in irradiated and non-irradiated distilled water are given in Figs. 1 and 2. The half-lives for the loss of individual PAHs determined on that basis are presented in Table 2.

Table 2. The half-lives of PAHs in distilled water, in days.

Conditions	Fit	B[b]F	B[k]F	B[a]P	I[c,d]P
Dark	83	47	43	26	42
Nitrogen purging	60	43	-	20	39
Aeration	63	18	16	8	7
Irradiation	39	17	15	6	7.5
Irradiation and aeration	26	10	9	4	5.5

The kinetic curves for the loss of PAHs in river water do not form straight lines. The example for the loss of PAHs in irradiated river water is given in Fig. 3. After an initial stage of rapid loss the process slowed down. Therefore, apart from the predicted half-life of fast stage $t_{1/2}^f$ (arbitrarily determined on the basis of initial loss rates), $t_{1/2}^s$ calculated for the slower stage has been given (Table 3). In this case the half life data should be considered only as estimates.

Relatively long half-lives were observed for Fit in distilled water ($t_{1/2} = 83$ days). The nitrogen purging, eliminating oxygen gave only slight acceleration of B[b]F, B[a]P and I[c,d]P loss. But a significant decrease, the fluoranthene half-life suggests that nitrogen purging could be a decisive factor for the removal of Fit from water. This is quite understandable because the partial pressure of Fit vapour ($6 \cdot 10^{-6}$ torr at 20°C) is nearly ten times higher than that of the other compounds [14].

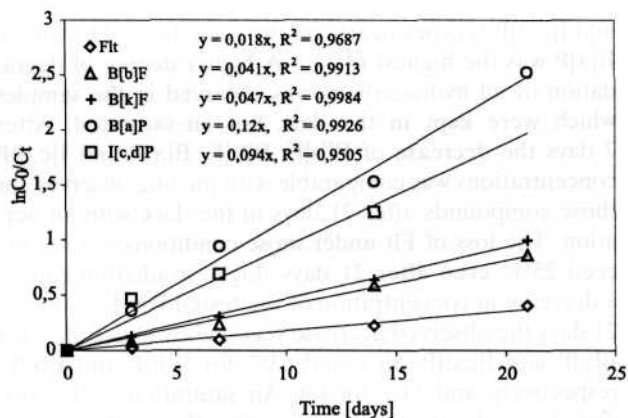


Fig. 1. First-order kinetic model for the loss of PAHs in distilled water; $t = 22^{\circ}\text{C}$, irradiation.

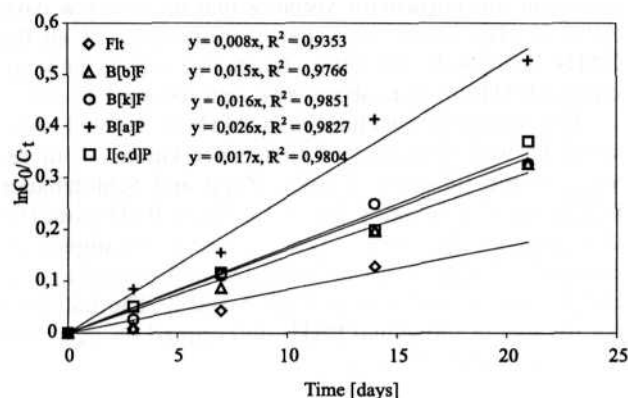


Fig. 2. First-order kinetic model for the loss of PAHs in distilled water; $t = 22^{\circ}\text{C}$, in dark.

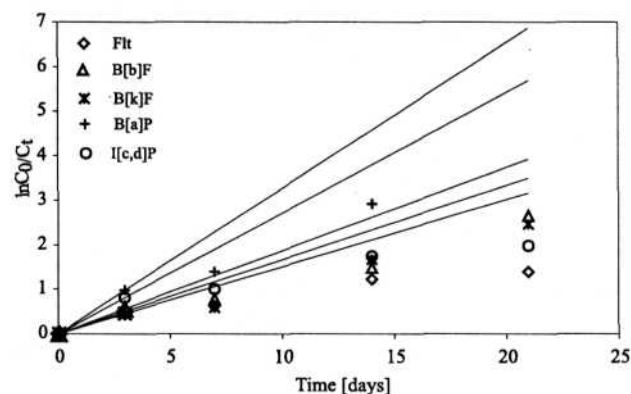


Fig. 3. First-order kinetic model for the loss of PAHs in river water; $t = 22^{\circ}\text{C}$, irradiation.

When air purging was used PAH loss was accelerated several-fold; however, it did not affect the half-life of Fit. It may be assumed that in these conditions the oxidation of PAHs occurred. The biggest loss was observed for B[a]P and I[c,d]P. Irradiation had the strongest effect on the loss rate of PAHs in the preliminary air-saturated water. Irradiation reduced the half-life values of PAHs

Table 3. The half-life of PAHs in river water, in days; f - fast stage, s - slow stage.

Conditions	Fit		B[b]F		B[k]F		B[a]P		I[c,d]P	
	f	s	f	s	f	s	f	s	f	s
Dark	12	53	9	26	-	-	11	16	5.5	25
Irradiation	4	13	3.5	5	4.5	5	2	3	2.5	10
Irradiation and aeration	3	4.5	3.5	4.5	3.5	4.5	1.5	4	3.5	7

from 2 to nearly 6 times. It should be noted that Fit was the most stable compound also under those conditions.

The rate of the concentration decrease of PAHs dissolved in river water was much higher than that observed in distilled water. In the dark even the half-life values in the slow stage were nearly two times lower than those obtained in the experiment with distilled water carried out under the same conditions. Irradiation of river water caused much higher loss rates of dissolved PAHs than in the case of distilled water. In river water the half-life of Fit decreased from 12 to 4 days in the fast stage and in the slow stage from 53 to 13 days, whereas it decreased only from 83 to 39 days in distilled water. Irradiation had a less varied effect on the stability of B[a]P - in distilled water the half-life decreased from 26 to 6 days, whereas in river water it decreased from 11 to 2 days in the fast stage and from 16 to 3 days in the slow stage. It may be assumed that the factor that intensifies the degradation of PAHs are photochemically produced oxidants (e.g. organic peroxy and peroxides, singlet oxygen, hydroperoxyl and hydroxyl radicals). Katz et al. [15] reported that the half-life of B[a]P in pond water decreased from 7.2 to 1.8 days in the presence of excess fulvic acid. In studies carried out in a controlled ecosystem enclosure the half-life of B[a]P was 3-4 days in water taken from a depth of 3 meters and 4-5 days in water from 7 meters [16]. For comparison, the half-life for free radical oxidation of B[a]P in air-saturated pure water was 4.3 days [17]. The results that we have obtained seem to confirm the interpretation proposed. But the rate of photodegradation of B[a]P in distilled water was over six times higher than the one for Fit, while in river water this rate was less than twice higher. Fluoranthene absorbs light at $\lambda_{max} = 277$ and 288 nm, whereas B[a]P at $\lambda_{max} = 297$ and 385 nm [12]. Thus, under the experimental conditions probably only direct photochemical reaction of B[a]P was preferential. Earlier, Zepp and Schlotzhauer [13] reported the half-lives for direct photolysis of Fit and B[a]P in inland water: 160 days and 3.2 days, respectively. Smaller differences in photodegradation rates observed for these compounds in river water indicate predominance of indirect photodegradation, e.g. in reaction with photochemically produced oxidants.

Obviously, not only photodegradation of PAHs, but also other light-induced processes taking place in natural waters may contribute to a decrease in the concentration of dissolved PAHs. This may be algae growth capable of adsorption on its surface or uptake of PAHs. In the experiments with irradiated river water there appeared a light green bloom on inside flask walls. However, a visible slowdown of the loss of dissolved PAHs suggests that

the role of this process is not dominant. As the rate of loss of PAHs dissolved in river water even in the slow stage is higher than the loss rate in distilled water, the slowdown of loss of dissolved PAHs in river water is associated by the authors with depletion of "easy" photochemically generated oxidants and/or adsorption of PAHs to colloidal particles. It may be expected that in real conditions the rate of photodegradation will additionally be affected by the presence of suspension, by attenuation of the passing light, but the suspension may also act as a photocatalyst, e.g. photooxidation of PAHs in the presence of TiO₂ [11]. On the other hand, the adsorption properties of particles will be mainly responsible for a decrease in the concentration of dissolved PAHs. In the Radomka river nearly 90% of PAHs occur in the adsorbed form [18].

Conclusions

The loss of PAHs aquatic concentrations was observed in each conditions, even in distilled water and in darkness. Much greater losses occurred in natural river water. The aeration with air or nitrogen increased the loss of PAHs. But the biggest degree of degradation of PAHs was noticed after irradiation, which suggests the occurrence of the photodegradation process. The loss of different PAHs was various. A higher degree of degradation was of B[a]P and I[c,d]P. It is very important especially for B[a]P, one of the most dangerous compounds to the environment.

Acknowledgement

This study was supported by the Polish Committee for Scientific Research, grant 0507/P04/99/16.

The authors would like to thank the anonymous reviewer for his/her constructive comments.

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